

Study of cement-fly ash paste exposed to sodium sulfate solutions with different concentrations at different temperatures

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Abstract

When concrete elements are partially exposed to sulfate environment, in the upper part of concrete elements above ground an aquiferous zone containing almost saturated and high pH value (>12.5) sulfate pore solution will be formed. The concentration of sulfate solution is much higher than 5%, as usually used in laboratory. It is necessary to study the performance of cement-fly ash paste in different high concentration sulfate solutions at different temperatures.

In this paper, pure cement paste and cement – fly ash (25% dosage) paste specimens were immersed in the 5%, 15%, 20%, 30%, 40% and 50% sodium sulfate solutions at 20 °C, 30 °C and 40 °C respectively. After 1, 3 and 6 months immersion, the compressive strength of the specimens was measured. XRD and thermal analysis were employed to analyze the reactive products of the paste. The experimental results show that the reactive aluminum in fly ash is activated by high concentration sodium sulfate solution at different temperatures and more ettringite is generated than pure cement paste.

1. INTRODUCTION

From the 1940s, PCA (Portland Cement Association) carried out a series of long-term field tests to study the performance of concrete partially exposed to sulfate environment [1-3]. One of the very important results was that the upper parts of blended concrete in contact with air were destroyed more severely than ordinary concrete. Another field test [4] also showed the same result. The researchers attributed salt crystallization to the cause for this appearance. However, according to microscopy results and theoretical analysis salt crystallization does not occur in hydrated cement paste [5-7]. There should be other reasons responsible for this appearance.

On the other hand, according to pore solution expression test results [7] an aquiferous zone containing almost saturated and high pH value sulfate pore solution can be formed in the upper parts of cement paste in contact with air. As we known, fly ash contains a large amount of reactive aluminum. Binders with an increased Al_2O_3 content can be more susceptible to the formation of ettringite. As an effective activator, Na_2SO_4 is often used to activate the pozzolanic reaction of fly ash and lime cement paste [8-10]. So, would the reactive aluminum in fly ash be activated in the high sulfate pore solution, resulting in more ettringite formation? In this paper, simulation tests were performed.

2. EXPERIMENTS

2.1 Raw materials

An ordinary Portland cement (CEM I 52.5 N), complying with EN 197-1 (2000), was used. Table 1 gives the chemical composition of cement and fly ash used in this study.

Table 1: Chemical composition of cement and fly ash (% by mass)

	CaO	SiO ₂	Fe ₂ O ₃	MgO	Al ₂ O ₃	SO ₃	CO ₂	Na ₂ O	K ₂ O	Ignition loss
Cement	62.21	19.12	3.79	0.86	5.39	3.06	0.72	-	-	1.65
Fly ash	4.46	53.31	7.53	2.45	26.43	0.9	-	1.15	0.9	4.0

2.2 Immersion test

The W/C ratio of the paste is 0.45. The dosages of fly ash were 25% by mass of cement replacement. Cement paste and cement + fly ash paste were cast in a mould with size of 20mm × 20mm × 60mm and moved into in a moist room After 4 to 6 hours, the paste was cut to cuboid specimens with size of 20mm × 20mm × 25mm in the mould. The specimens were demolded after 24 hours, and then cured in water at 20 degree for 28 days. After curing, the specimens were moved out and dried in a climate room at 20°C±2°C and 60%±5% RH for one week. The specimens were placed in plastic bottles with two tight lids, and different concentration sodium sulfate solutions were irrigated into the bottles until all of the specimens were surrounded. Then, the bottles were placed put in the plastic tank containing water. The water was heated and the temperature was kept at 30 °C or 40 °C by a control system. Other bottles were place in the climate room at 20°C±2°C. The exposure conditions are shown in Table 2. At 1, 3 and 6 months exposure age, the compressive strength of the specimens (6 specimens for one group) was measured. XRD and thermal analysis were employed to identify reaction products.

Table 2: Exposure conditions and number of specimens at 20, 30, 40 °C

Temperature	Concentration (g/100g water)					
water						
20 °C	5	15	20			
30 °C	5	15	20	30	40	
40 °C	5	15	20	30	40	50

3. RESULTS

3.1 Development of compressive strength of cement paste and cement + FA paste

Figure 1 to Figure 6 shows the development of compressive strength of cement paste and cement +FA paste. According to theses results, a clear pathway for strength development can be observed. After short time exposure, the cement + FA paste shows lower strength than cement paste. With the progress of exposure, and with the increase of temperature and concentration, the strength of cement + FA grows and exceeds it of cement pastes. At last, after a longer period of exposure, the strength of cement + FA decreases and is lower than cement paste again.

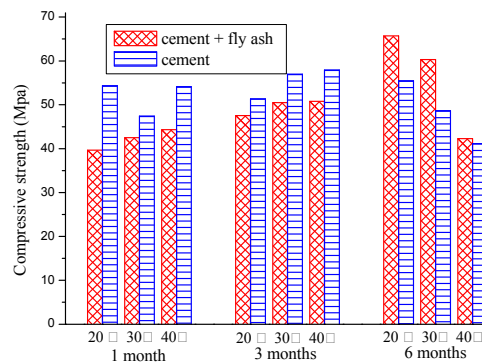


Figure1: Development of compressive strength of pastes in the 5% Na₂SO₄ solution

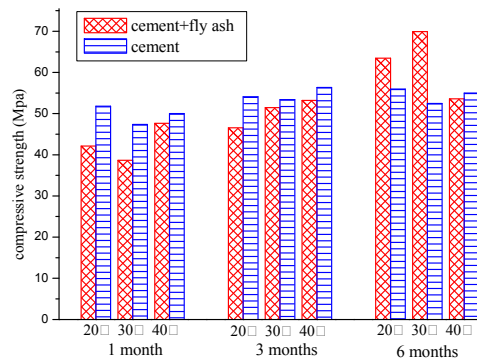


Figure 2: Development of compressive strength of pastes in the 15% Na₂SO₄ solution

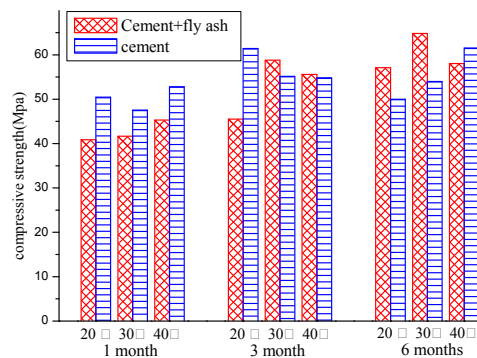


Figure 3: Development of compressive strength of pastes in the 20% Na₂SO₄ solution

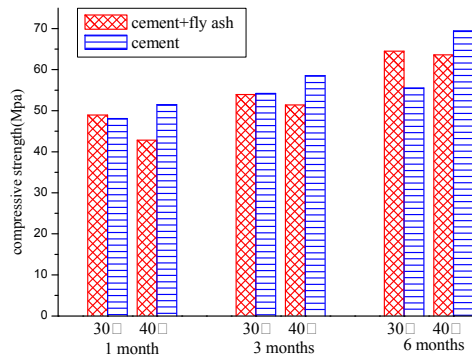


Figure 4: Development of compressive strength of pastes in the 30% Na₂SO₄ solution

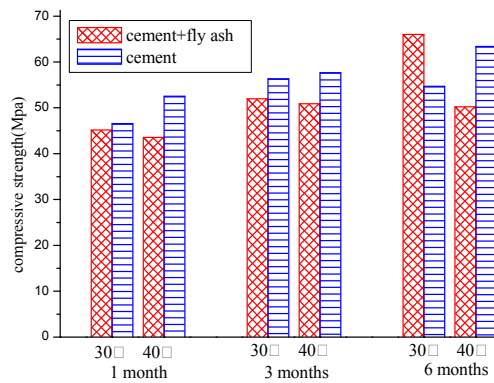


Figure 5: Development of compressive strength of pastes in the 40% Na₂SO₄ solution

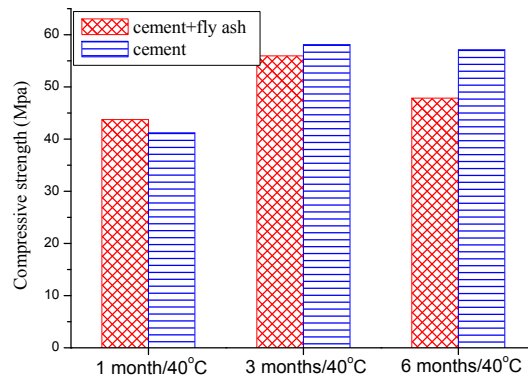


Figure 6: Development of compressive strength of pastes in the 50% Na₂SO₄ solution

3.2 XRD analysis and thermal analysis

List of symbols in XRD patterns:

P: Portlandite, calcium hydroxide – Ca(OH)₂

C: Calcite – CaCO₃

E: Ettringite Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O

L: Larnite- Ca₂SiO₄

M: Mullite- Al₈Si₂O₁₃

CA: Calcium AluminumOxide Hydrate Ca₄Al₂O₇·xH₂O

S: Quartz-SiO₂

V: Vaterite- CaCO_3

The following XRD patterns and thermal analysis curves exhibit the reaction products of paste in different high concentration sodium sulfate solutions at different temperatures.

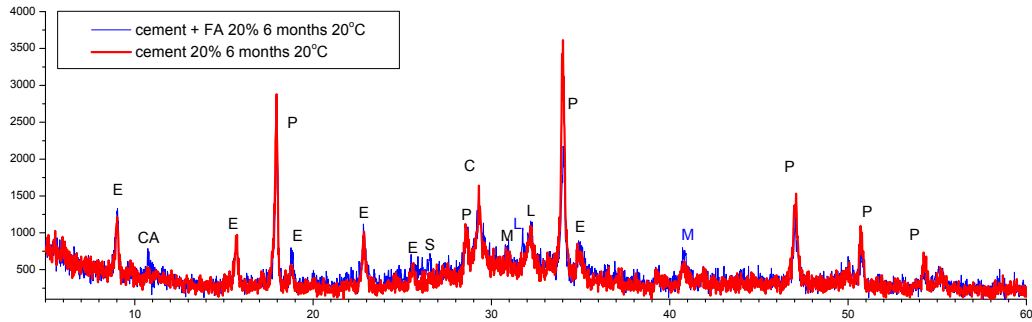


Figure 7: XRD patterns of cement paste and cement + FA paste in 20% Na_2SO_4 solution at 20 °C for 6 months

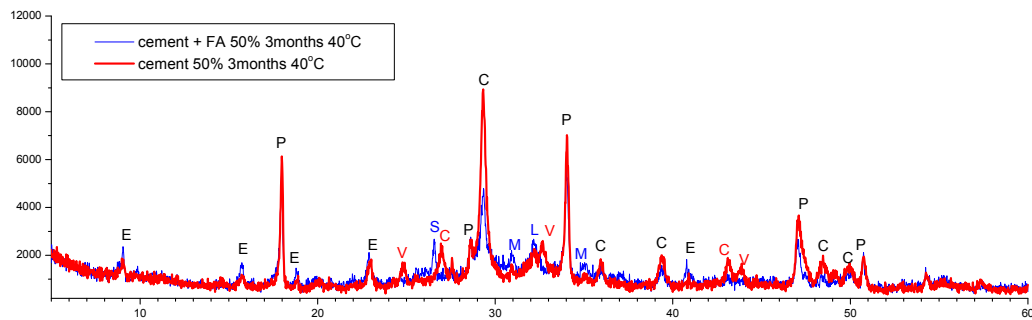


Figure 8: XRD patterns of cement paste and cement + FA paste in 50% Na_2SO_4 solution at 40 °C for 3 months

A clear difference in ettringite peaks in the XRD patterns of cement paste and cement + FA paste is observed. In the higher concentration sodium sulfate solutions at higher temperature, more ettringite is generated in cement + FA paste.

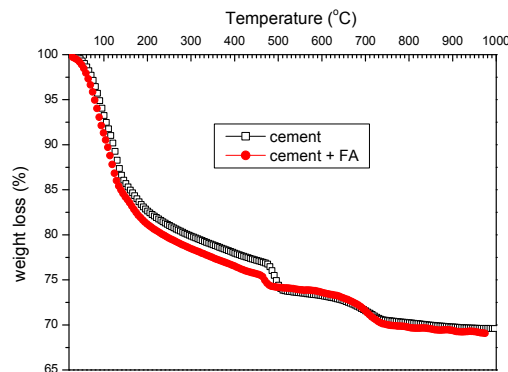


Figure 9: TGA of paste in 5% sodium sulfate solution at 30 °C for 6 months

The TGA curve can quantitatively provide the weight loss of each individual phase. For the interpretation of TGA and DTG results, research [11] pointed out that the weight loss of ettringite at 50-110 °C.

Figure 9 shows the TGA curves of cement paste and cement + FA paste in 5% sodium sulfate solution at 30 °C for 6 months. 7.54% and 9.11% of weigh loss at 50 – 110 °C can be calculated for cement paste and cement + FA paste. The total weigh of the cement paste sample was 13.0 mg and 19.2 mg for the cement + FA paste. The total amount of water escaping from ettringite in cement paste was 0.98 mg, while it was 1.75mg in cement + FA. The amount of ettringite in cement paste and cement + FA paste was 2.8 mg and 5.0 mg respectively based on the water loss corresponding to 20 H₂O. These results indicate even in 5% sodium sulfate solution more ettringite can be generated at 30 °C.

Figure 10 and Figure 11 show the TGA and DTG curves of cement paste and cement + FA paste immersed in 30% sodium sulfate solution at 30 °C and 15% sodium sulfate solution at 40 °C for 6 months.

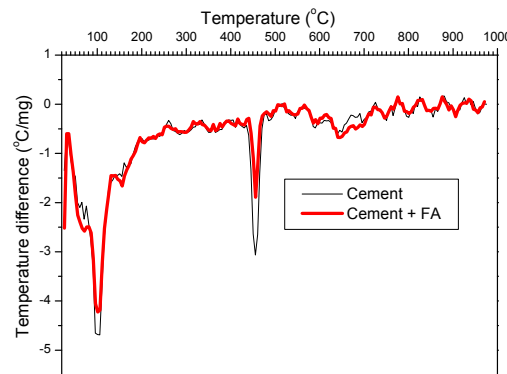


Figure 10: DTG of cement paste and cement + FA paste partially immersed in 30% sodium sulfate solution at 30°C for 6 months

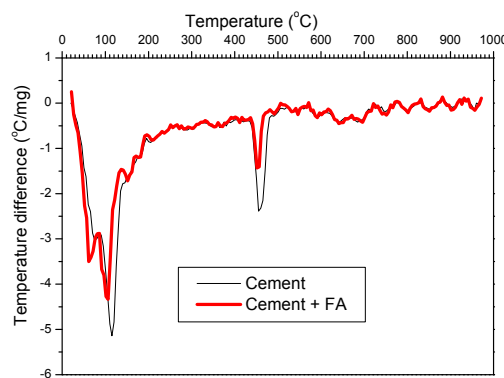


Figure 11: DTG of cement paste and cement + FA paste partially immersed in 15% sodium sulfate solution at 40°C for 6 months

Obviously, a stronger peak can be found at 50 – 110 °C for cement + fly ash paste in comparison with cement paste. This means that more ettringite was formed in the cement + FA paste than in the cement paste.

3.3 Discussion

Concerning to the role of mineral additions in the sulfate performance of cementitious materials, hundreds and thousands of previous researches all supported that mineral additions, such as fly ash, slag powder, silica fume and metakaolin, play a positive role in making sulfate-resisting concrete, independent from the exposure conditions (sodium sulfate, magnesium sulfate, or ammonium sulfate). It seems that mineral pozzolan additions are a kind of general remedy for making sulfate resistant concrete. In the 1960s and 1970s extensive studies at the U.S. Bureau of Reclamation [12] showed that concretes containing 30 percent low-calcium fly ashes showed greatly improved sulfate resistance to a standard sodium sulfate solution. However, the use of high-calcium fly ashes generally reduced the sulfate resistance. High-calcium fly ashes containing highly reactive alumina in the form of C_3A or $C_4A_3\hat{S}$ are therefore less suitable than low-calcium fly ashes for improving the sulfate resistance of concrete. Taylor also pointed out [13, 14] that if slag has low alumina content, it improves the sulfate resistance, but with a high content of alumina, the reverse is the case. Bellmann [15] also pointed out that it should not be overlooked that fly ash can contain a large amount of reactive aluminum and that binders with an increased Al_2O_3 content can be more susceptible to the formation of ettringite.

The fly ash particles consist of glassy spheres and possess little or no pozzolanic activity to react with calcium hydroxide. It needs some methods to activate, such as thermal activation, mechanical activation and chemical activation [8]. As to the chemical activation, as an effective activator, Na_2SO_4 is often used to activate the pozzolanic reaction of fly ash cement paste. Shi [9, 10] indicated that the addition of Na_2SO_4 to lime and natural pozzolan paste accelerates the pozzolanic reaction and results in the formation of AFT (ettringite). The range of addition of sodium sulfate anhydrite was 0 - 5% by the mass of cementitious materials. Previous research [7] already showed that a high concentration sulfate pore solution zone under efflorescence could form in the pastes. The content of sulfate in the solution was much higher than 5% and almost reached the solubility of sodium sulfate at 20 °C. It should be noted that the temperature in laboratory research is always at 20 °C. However, due to wick action, the concentration will also grow with increasing temperature. The above experiment showed that even in 5% sodium sulfate solution more ettringite could be formed in the cement + fly ash paste if the exposure temperature was at 30 °C. In higher concentration sodium sulfate solution at higher temperature, much more ettringite was formed in the cement + fly ash paste than in plain cement paste. With the progress of sulfate attack, the sulfate resistant performance of cement + fly ash paste becomes worse than for pure cement paste.

5. CONCLUSIONS

From the experimental results, the pozzolan potential of fly ash can be activated in high sodium sulfate solution at different temperatures, and more ettringite can be generated. This is thought to be the main reason causing more severe damage of fly ash concrete partially exposed to sulfate environment.

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